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LUBRICANTS QUALITY ANALYSIS SYSTEM DEVELOPMENT

INTERIM REPORT
BFLRF No. 293

Volume II
Chemical Characterization of Lubricants

By

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13. ABSTRACT (Maximum 200 words)

Major phases of this study included providing the results, critical evaluation, and implications of a literature search in a "white paper" on advanced analytical methodology for mobility fuels and lubricants applications, assessment of a commercial used engine oil evaluation methodology, and analysis and characterization of new lubricants. In assessing a commercial used oil analysis method, it was concluded that this FTIR-based used oil analysis method should be used only for trend analysis in which the lubricant and the fuel are known and controlled.

Efforts were made to characterize and identify lubricants through instrumental analyses, including high-temperature gas chromatography, gel permeation chromatography, elemental analysis, spectroscopic fingerprinting, and establishing FTIR spectral libraries. To increase usefulness of the results of libraries of FTIR spectra, data bases have been constructed to include all known specification and inspection data. Calibration curves were established to measure several major lubricating oil additive concentrations in a lubricant base stock, through their FTIR responses. Several increasingly complex experimental protocols are suggested, depending upon the source of lubricant and the needed lubricant property requirements. While a final experimental protocol has not yet been established, a tentative analytical chemical protocol was developed. Present experimental protocol does not address the detection and destruction of antimaterial agents.

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EXECUTIVE SUMMARY

Objectives: The objective of this program was to initiate development of a rational experimental protocol for the assessment of the quality of new and used lubricating oils through instrumental chemical analysis.

Importance of Project: To assure reliable and rapid response to problems related to the quality of mobility fuels and lubricants, state-of-the-art analytical instrumentation is essential. This report summarizes the use and potential use of leading edge technologies for the characterization of lubricants.

Accomplishments: Major phases of this work included (a) assessment of a commercial used engine oil evaluation methodology, (b) preparation of a white paper on advanced analytical methodology for mobility fuels and lubricants applications, and (c) analysis and characterization of new lubricants.

In assessing a commercial used oil analysis method, it was concluded that this Fourier transform infrared (FTIR)-based used oil analysis method should be used only within the scope of its design, i.e., for trend analysis in a well-regulated fleet of vehicles in which the lubricant and the fuel are known and controlled. Since these criteria are not fulfilled under normal field operations, and especially under battlefield conditions, this commercial analytical method should not be used by the U.S. Army, since furnishing misleading data under any condition is considered worse than providing no data at all. If this commercial program is to be used under nontrend analysis conditions, that is, conditions for which it was not designed, the program must be modified. The software may be used only if samples of the new lubricant and the specific fuel used in the vehicle are used as appropriate spectral reference materials. It is unlikely that such samples will be available from Army vehicles under battlefield conditions. However, if these inputs were accessible to the program, the computer may calculate data useful in aiding engine maintenance.

The necessity of the white paper became obvious as a result of feedback on lessons learned during the 1991 Operations Desert Shield and Desert Storm, through several related communications, and through a concept requirement of the U.S. Army Quartermaster School. These documents expressed the urgent requirement to identify equipment that can assess the quality of fuels and lubricants in or near battlefield conditions. To develop a solid foundation for analytical chemical requirements for the U.S. military forces, a literature search was initiated. Results, critical evaluation, and implications of the literature search were summarized in Interim Report BFLRF No. 273, entitled "Advanced Analytical Methodology for Mobility Fuels and Lubricants Applications." The report includes extensive literature references, definitions, an abbreviated discussion of the available methodologies, and the classification of these methodologies.

Efforts were made to characterize and identify lubricants through instrumental analyses, including spectroscopic fingerprinting and establishing FTIR spectral libraries. To increase the usefulness of the results of libraries of FTIR spectra, data bases have been constructed to include all known specification and inspection data. If FTIR spectra of all possible acceptable lubricant samples

were to be included in a spectral library, any later generation sample of the same lubricant may be properly identified by simply establishing spectral identities through library searches.

Calibration curves were established to measure lubricating oil additive concentrations in a solvent refined 150 neutral base stock, from their FTIR absorbance responses. The studied lubricating oil additives included samples of zinc primary dialkyl dithiophosphate, zinc secondary dialkyl dithiophosphate, calcium alkyl phenate, calcium alkylbenzene sulfonate, sodium alkylbenzene sulfonate, magnesium alkylbenzene sulfonate, polyisobutyl succinimide succinate ester, and polyisobutyl succinimide.

Several increasingly complex experimental protocols are suggested to characterize these products, depending upon the source of lubricant and the needed lubricant property requirements. While a final experimental protocol has not yet been established during the course of this project, a working or tentative analytical chemical protocol was developed and is being upgraded as new information warrants.

In the present most complex experimental protocol, the analysis of the various products includes elemental analysis, midband FTIR spectroscopy, high-performance liquid chromatography (HPLC) in its gel permeation chromatographic (GPC) mode, and high-temperature gas chromatography (HTGC). This integrated set of instruments would be operated, and the results evaluated by a dedicated on-board computer, requiring only minimal interfacing with a petroleum laboratory specialist. Alternately, the raw data from the instrument cluster may be transferred through electronic satellite, e.g., linkage to a central processing facility, which would then return the processed data to the military commander.

Present experimental protocol does not address the detection and destruction of antimaterial agents. Such analyses require highly specific knowledge of the possible agents, followed by design of specific analytical tools to detect them.

<u>Military Impact</u>: Described analytical instruments would provide the field commanders with the necessary data about the suitability of petroleum, oils, and lubricants (POL) products for any given mission and would allow the determination of reasoned recommendations for proper applications in the shortest time possible.

FOREWORD/ACKNOWLEDGMENTS

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I. INTRODUCTION

The drive to make modern military equipment more proficient has resulted in the use of more complex and expensive components with critical and exacting requirements. A major requirement for the operation and maintenance of such equipment is an adequate supply of the proper fuel and lubricant. To assure reliable and rapid response to problems related to the quality of mobility fuels and lubricants, state-of-the-art analytical instrumentation is essential. Such analytical instruments will provide the field commanders with the necessary data about the suitability of petroleum, oil, and lubricant (POL) products for any given mission and will allow the deduction of reasoned recommendations for proper applications in the shortest time possible.

Thus, there is a strong need to develop analytical chemical methodology and equipment capable of ensuring quality control of petroleum products in or near battlefield conditions. This equipment, which should be transportable and, perhaps, portable, will permit the timely assessment of the quality of fuels and lubricants at Army facilities. The use of this equipment would identify specific POL products and determine their compliance with the respective specifications. If needed, recommendations for corrective actions would be provided by the expert system associated with the analytical equipment. Such systems may also identify host nation, commercial, or unknown source POL products that may be used in lieu of fully acceptable lubricants, i.e., those identified in a qualified products list (QPL), either as an alternative or as an emergency lubricant.

Traditional quality assurance and quality conformance analyses of petroleum products in the field are described in MIL-HDBK-200G.(1)* This handbook defines the specification and use limits for various products and the acceptable analytical procedures that must be implemented by "properly trained personnel ... to protect original product quality." Selection of tests for this handbook was moderated by the availability of simple, traditional, and historical procedures that were available for military applications. In the integrated future military petroleum laboratory system, some of the traditional test procedures are expected to be retained. Other procedures will

* Underscored numbers in parentheses refer to the list of references at the end of this report.

be replaced by newer methodologies that would provide improved speed, reliability, and more meaningful input about the usefulness and limitations of such products.

The fast growing science of artificial intelligence (2) and the development of expert systems (3,4) are expected to be integral parts of this methodology to provide substantial improvements in advanced analytical chemistry, including those used by the military.

II. OBJECTIVE

The objective of this program was to initiate development of a rational experimental protocol for the assessment of the quality of new and used lubricating oils through instrumental chemical analysis.

III. DISCUSSION

Project activities encompassed several phases: determination of the quality of used oils by Fourier Transform Infrared (FTIR) spectroscopy; preparation of a white paper on available methodologies for the analysis of petroleum products, and how these methodologies may be utilized by the military under and near battlefield conditions; analysis of new lubricants; and development of correlations between FTIR spectroscopic data and the data measured by traditional chemical and physical methods.

A. Used Oil Analysis

Evaluation of remaining useful life of used engine oils requires the application of several chemical and instrumental analytical methods in order to address the various aspects of lubricant composition. Analysis is then followed by consolidation of all data to derive an increasingly complete description of the state of the lubricant. Some of the more commonly used methods of used engine oil analysis are elemental analysis to determine additive and wear-induced metal

content; ferrography to identify wear particles; chemical analysis to determine the acidity and remaining basicity (buffer capacity) of the lubricant through determination of the total acid number and total base number values; and midband FTIR spectroscopy to establish historical "fingerprinting" of the lubricant, to determine the presence of and possibly to measure additive components, and to follow compositional trends in the condition of lubricants during engine operation.

During this program, the scope and limitations of a commercially available method of used engine oil analysis, based on FTIR spectroscopy, were evaluated for military field applications. This commercial product, marketed by Nicolet Instrument Company, was jointly developed by Nicolet and Caterpillar, Inc. for trend analysis of used oils. The instrument provides information on oil contamination by soot, oxidation, nitrogenation, and sulfation, and by fuel, glycol, and water dilution.

The Belvoir Fuels and Lubricants Research Facility (BFLRF) study did not evaluate the usefulness and validity of the program for trend analysis, but attempted to determine the scope of the method for its possible use under nontrend analysis conditions, such as those that exist under usual military field, and especially battlefield, conditions. The BFLRF study (5) included partial evaluation of the instrument's output for the effects of (a) using the auto reference feature of the program, (b) increased soot content on other measured properties, (c) addition of makeup oil, and (d) fuel composition on fuel dilution data.

The following conclusions were reached:

a. The auto reference feature of the program may possibly be useful under specialized conditions; however, without confirming evidence, the program may yield misleading results.

b. Carbon black loading in used oils did affect the analytical results of other measured contaminants. Increased amounts of carbon black decreased the infrared transmittance

through the oils and increased the apparent absorbance of peaks used to measure oxidation, nitration, sulfation, and water content.

c. Oil dilution (makeup oil) with new oil from the same origin as the used oil lowered the contaminant levels in a linear manner, as expected. If, however, the results were derived without specifying the reference oil, the software-selected reference oil occasionally indicated grossly false fuel dilution values.

d. The study showed the sensitivity of this commercial FTIR procedure to the aromatic hydrocarbon content of the fuel and its effect on fuel dilution values. Oil diluted with fuel containing high concentrations of aromatic hydrocarbons resulted in higher than actual fuel dilution values. Conversely, when oil was diluted with high concentrations of fuel containing low concentrations of aromatic hydrocarbons, fuel dilution values below detectability limits were measured. For example, actual fuel dilution of 8 percent registered as "less than 2 percent." These observations are especially relevant with the introduction of the recently mandated low-aromatic hydrocarbon- (and sulfur) containing diesel fuel.

e. It was concluded that this FTIR-based used oil analysis method should be used only within the scope of its design, i.e., for trend analysis in a well-regulated fleet of vehicles in which the lubricant and the fuel are known and controlled. Since these criteria are not fulfilled under normal military field operations, and especially under battlefield conditions, this program should not be used by the U.S. Army. It is felt that furnishing misleading data under any condition is <u>worse</u> than providing no data at all. If this program is to be used under nontrend analysis conditions, i.e., conditions for which it was not designed, the program must be modified. The software may be used only if samples of the new lubricant and the specific fuel used in the vehicle are used as appropriate spectral reference materials. While it is unlikely that such samples may be available from Army vehicles under battlefield conditions, if these inputs were accessible to the program, the computer may calculate useful data to aid engine maintenance.

B. White Paper on Advanced Analytical Methodology for Mobility Fuels and Lubricants Applications

As feedback on lessons learned during the 1990-1991 Operation Desert Shield-Desert Storm, several communications (6–9) expressed the urgent requirement to identify equipment that can assess the quality of fuels and lubricants in or near battlefield conditions. The equipment should perform relatively fast, be simple to operate, and preferably be commercially available. To develop a solid foundation for analytical chemical requirements for the U.S. military forces, a literature search was initiated. Results, critical evaluation, and implications of the literature search were summarized in Interim Report BFLRF No. 273, entitled "Advanced Analytical Methodology for Mobility Fuels and Lubricants Applications."(10) The report includes extensive literature references, definitions, an abbreviated discussion of the available methodologies, and the classification of these methodologies.

To satisfy a concept requirement of the U.S. Army Quartermaster School (11), Reference 10 was prepared to include classification of analytical chemical requirements that provide increasingly more detailed and more precise, albeit more complex, analytical data at the tactical, operational, and theater level applications:

a. Tactical testing at forward areas, where equipment should be man-portable to aid fast and simple "go" or "no-go" decisions. Operation of such equipment should require a minimum level of training.

b. Operational testing allows the use of a limited number of tests performed on sophisticated, transportable equipment. Operators of this equipment would be "school-trained petroleum laboratory specialists" who would perform the tests, and through an interactive computer program, interpret results and provide expert opinions on petroleum products. Due to increased capability and sophistication, such laboratories would be able to provide improved precision and reliability of data and recommendations. The analytical equipment would be housed in trailers or transportable modules.

c. Theater level testing would provide the most comprehensive analyses, interpretation, and recommendations for the commanders. In this area, analyses of petroleum products would be performed using a battery of state-of-the-art equipment, interfaced with computer-based expert systems, possibly even using communications through satellite linkage. This level of testing would be performed in portable shelters.

Basic criteria for selection and evaluation of equipment and procedures for the present purposes, in decreasing order, are:

- Provide critical information
- Reliability
- Ease of operation
- Portability
- Requirements for operator with low skill level
- Short analytical time
- Low requirements for maintenance and calibration
- Reasonable equipment cost.

Some of the present commercially available instruments are bulky, may require special handling, and possibly require special cooling systems. Examples of such instruments are elemental analyzers, e.g., the inductively coupled plasma (ICP) and energy-dispersive X-ray fluorescence (XRF) spectroscopes. While ruggedization of equipment is possible, such instruments are not expected to be useful below the theater level of operation.

Commercially available instruments begin to show substantial capability and adaptability to provide a variety of desirable data for military applications. Such systems may still require extensive modifications and preliminary calibrations before they may be acceptable for military applications. The preliminary calibrations may then be stored in the spectroscope's memory. An example of such technology utilizes the principles of midband FTIR and near-infrared (near-IR) spectroscopies.

The following listing classifies the various instrumental analytical methods that may be considered:

a. Equipment and procedures that determine the composition of fuels, lubricants, their additives, and their degradation products;

b. Equipment and procedures that determine composition, which, in turn, may be correlated to specific inspection requirements and performance characteristics;

c. Equipment and procedures that directly determine inspection property requirements and performance characteristics.

Diverse technologies will have to be applied and their data integrated into a coherent description of lubricants. The following thoughts are offered for consideration:

Equipment and procedures that determine the composition of fuels, lubricants, their additives, and their degradation products:

- Elemental analysis
- FTIR spectroscopy
- Ultraviolet and visible (UV/VIS) region spectroscopy
- Gas chromatography (GC)
- Gas chromatography coupled with mass spectroscopy (GC/MS)
- High-performance liquid chromatography (HPLC)
- Nuclear magnetic resonance (NMR) spectroscopy.

Equipment and procedures that determine composition that, in turn, may be correlated to specific inspection requirements and performance characteristics:

- Elemental analysis
- FTIR spectroscopy

- UV/VIS
- GC
- GC/MS
- NMR spectroscopy
- Thermal gravimetric analysis (TGA)
- Differential scanning calorimetry (DSC).

Equipment and procedures that directly determine inspection property requirements and performance characteristics:

- Elemental Analyzer
- Gravity Meter
- Viscometer
- Sulfur Analyzer
- Infrared Analyzer (working in the more sensitive fundamental resonance frequency range of approximately 4000 to 400 cm^{-1}).

The report also summarized the military analytical requirement challenges for chemists, for computer scientists, and equipment manufacturers to modify existing systems, or, when needed, to develop new systems and experimental protocols. These challenges of and directions in modern analytical chemistry may be summarized as follows:

a. Product properties of interest and possible analytical chemical requirements must be defined. Although requirements of the present MIL-HDBK-200G may be kept and adapted to include modern analytical instrumentation, present and future studies may lead to new scopes of analytical needs as they relate to the needs of the future military commanders.

b. Compositional complexity of petroleum products may pose substantial barriers that need to be reduced by fractionation to ease analysis and characterization. This fractionation must be accomplished without uncontrolled alterations, modifications or

loss of some of the components that comprise the sample. It has been shown for example, that, during some chromatographic manipulations of certain lubricant additives and fuel decomposition products, some components are altered. Additionally, some fuel and lubricant components may be irreversibly adsorbed on the adsorbent. Subsequent chemical analysis of the product, therefore, yields incomplete and questionable results. Reduction of sample complexity must be accomplished on a quantitative basis while continually demonstrating that the results actually refer to the original sample in question.

c. The chosen set of analytical method must yield unique analytical data that would allow deducing reasoned conclusions about the sample. To achieve these goals, development of new analytical chemical protocol for the rational and expedient analysis of fuels and lubricants is necessary.

d. Correlation must exist, or should be developed, between the results of the analytical chemical data and performance parameters that characterize the sample.

e. Management and interpretation of the analytical data are becoming increasingly simplified as new generations of computerized instrumentation gain power and sophistication. Traditionally, the data generated by experiments or by instruments have been collected, manipulated, and interpreted by appropriately trained personnel. Now, most modern analytical instruments contain suitable computer(s) to control the operation and calibration of the instrument and help reduce the data into a useful, reportable format. These computers ease the burden on the personnel in generating increasing amounts of highly sophisticated data. The computers may (a) govern operation of a set of instruments, (b) integrate data from various instruments and other sources, and (c) convert raw data into information. Such information may be easily and automatically evaluated by comparing it to computer-based specification requirements. When sufficient information is available, the computers may also provide some measure of interpretation and indication of practical implications of the acquired data.

f. Expert systems that not only interpret data of a single instrument, but would automatically draw well-reasoned conclusions from results obtained by a battery of analytical methodologies, are still to be developed.

Development of "expert systems" requires input from several sources. Input is required from professional staff who (a) develop and use these analytical methods and techniques and interpret the results of the various measurements, (b) compile, and where needed, develop additional laboratory test versus performance correlations, (c) are involved with the development of analytical instrumentation, and (d) are computer experts capable of combining the reasoning of the multitude of experts into a coherent computer program.

C. Analysis of New Lubricants

1. General Considerations

For a number of reasons, chemical analysis of new lubricants is a formidable task even for highly trained professional staff in a specialized, dedicated laboratory. As with any petroleum product, the raw lubricants, or base stocks, are complex mixtures of compounds, including hydrocarbons of various classes and a variety of polar organic compounds that may contain the elements of oxygen, sulfur, nitrogen, etc. Composition of base stocks may vary according to their crude oil source, refining processes, and viscosity grades. To achieve a desired level of performance from a "finished" lubricant, several base stocks may be blended and modified by a wide variety of performance-enhancing proprietary additives. Each of the additives may be present from trace quantities up to several percent in concentration.

Such diversity and chemical complexity of a petroleum-based lubricant's composition mandates the use of several sophisticated analytical techniques. To arrive at a reasonable solution, the following challenges of modern analytical chemistry must be fulfilled:

a. Analytical chemical needs must be defined, i.e., key lubricant properties that must be identified;

b. Where needed, complex mixtures must be separated into fractions that are simple enough to yield unique analytical data by the various analytical techniques;

c. Results of the various analytical chemical data must be combined to arrive at reasoned conclusions about the sample;

d. The integrated analytical chemical data should be correlated with performance parameters that characterize the sample.

Such complex analyses cannot be performed, nor are they recommended, for routine military field applications. The following paragraphs describe methodologies that offer compromises that may still yield useful information for the military field commander.

2. Identification of Lubricants Using Fourier Transform Infrared (FTIR) Spectroscopy

As discussed previously, true chemical analysis of lubricants was not deemed feasible under current project objectives. Instead, efforts were made to characterize and identify lubricants through instrumental analyses, including spectroscopic fingerprinting. FTIR spectra of finished products were obtained to build a library of lubricants whose members could be identified at a later date through matching of property values and establishing spectral identities. To achieve these goals, a large number of military automotive lubricants were obtained. Products were procured under MIL-L-2104E, MIL-L-2105D, and MIL-L-21260D specifications. Several samples were also supplied under the now obsolete MIL-L-46152E. The data base comprises over 600 samples of finished lubricants, 38 various base stocks, and 22 single and combination samples of additives, or additive packages.

Libraries of FTIR spectra were established to incorporate a combination of all finished lubricants, base stocks, additives, and additive packages. To increase ease of categorization, individual

libraries that contained the separated classes of (a) base stocks, (b) additives and additive packages, and (c) finished products were also established.

Spectral library search is based on comparing the spectrum of an unknown sample with each of the known (reference) spectra of the library. This comparison is the result of spectral subtraction. The fewer the differences, the better the match between the newly measured and the library spectrum. The best match is that with the least number of differences. Spectral searches may be performed using various algorithms, depending on sample and spectral properties. *Absolute difference* algorithm can distinguish subtle differences between spectra that are similar and that contain few unique features. Such a search is sensitive for proper baseline correction. *Absolute derivative* algorithm computes the difference between the first derivatives of the unknown sample and the library files. This search minimizes the effects of sloping baselines, band shapes, and sample handling. *Squared difference* algorithm is used when searching a noisy spectrum. This square of difference algorithm is similar to the absolute derivative searches, but is more useful in cases where the signal-to-noise ratio is low as it minimizes the differences in background noise in the spectra. Due to the good quality of the lubricant spectra in this program, the best search results were obtained using absolute derivative algorithm.

It was demonstrated that any sample may be identified, i.e., found as a result of computer search, if it were already part of the library. If, therefore, FTIR spectra are generated of all possible qualified lubricants of interest, then a new sample of any one of these lubricants may be matched to the originally qualified product. If any part of the lubricant were changed, e.g., the additive package or lubricant base stocks were altered, the FTIR will show an increased number of differences between the original library sample and the unknown sample, resulting in not finding a match or showing only similarity instead of identity between the samples.

If, therefore, FTIR spectra of all possible acceptable lubricant samples are included in a spectral library, any later generation sample of the same lubricant may be properly identified by simply establishing spectral identities through library searches.

To increase usefulness of the results of libraries of FTIR spectra, these data bases have been assembled that include all known specification, composition, and inspection data. The purpose of setting up the data base was to be able to immediately combine the FTIR library search results on each available lubricant with the associated data, and, using computerized expert systems, provide reasoned recommendations for the user. The data bases were established using Borland's "Paradox," version 3.5 software package. Where information was available, the following data were entered in the data base:

- Sample source
- Product identification
- Military specification number(s)
- QPL number
- FTIR identification number
- Limited compositional information
- Elemental analysis for S, P, Zn, N, Ca, Mg, B, Cu, Cl, Na
- High-temperature gas chromatographic distillation data
- Molecular size distribution data from gel permeation chromatography
- Kinematic viscosity at 40°C
- Kinematic viscosity at 100°C
- Viscosity index
- Total base number
- Density
- Pour point
- Stable pour point
- Flash point
- Sulfated ash.

3. Correlation of Lubricant Properties With FTIR Spectra

Only limited study was performed to correlate FTIR spectral information with usual inspection properties of lubricants. Correlations were attempted to included sulfur contents and total base

number data. While minor correlations were observed between sulfur content and FTIR spectra, the expected FTIR correlations with base number values were not yet established. Possible reasons for this apparent lack of correlation may be (a) the complexity of the sample, (b) low extinction coefficients associated with pertinent FTIR peaks, (c) necessity for modification of the examined spectral regions, and (d) large property value changes that may be due to relatively low concentrations of additive(s).

In view of the substantial success that has been achieved in extracting infrared spectral information that correlated with properties of hydrocarbon fuels (12,13), several conventional lubricant property values are expected to be amenable to successful modeling and estimation through midband FTIR spectroscopy. Such objectives should be addressed in further studies.

4. Quantitative Analysis of Lubricating Oil Additives by FTIR

Industrial samples of eight, nominally single additives, commonly used in MIL-L-2104E lubricants, were obtained. FTIR spectra were obtained on each of these additives in its carrier oil. Spectra of the base stock and the additives are shown as Figs. 1 through 9. For comparison, the FTIR spectrum of a solvent-refined neutral base stock is also shown. Generic description of these samples, their BFLRF-assigned identification names, and their figure numbers are summarized below:

Additive ID	Figure No.	Sample Description
1081BC	1	Solvent-refined 150 neutral base stock
1107SA	2	Zinc primary dialkyl dithiophosphate (Prim. ZDDP) (oxidation and corrosion inhibitor, antiwear additive)
1108SA	3	Zinc secondary dialkyl dithiophosphate (Sec. ZDDP) (oxidation and corrosion inhibitor, antiwear additive)
1110SA	4	Calcium alkylbenzene phenate (dispersant antioxidant, corrosion inhibitor)
1109SA	5	Calcium alkylbenzene sulfonate (metallic dispersant, antioxidant, corrosion inhibitor)
1111SA	6	Sodium alkylbenzene sulfonate (metallic dispersant, antioxidant, corrosion inhibitor)
1114SA	7	Magnesium alkylbenzene sulfonate (metallic dispersant, antioxidant, corrosion inhibitor)
1112SA	8	Polyisobutyl succinimide/succinate ester (ashless dispersant)
1113SA	9	Polyisobutyl succinimide (ashless dispersant)

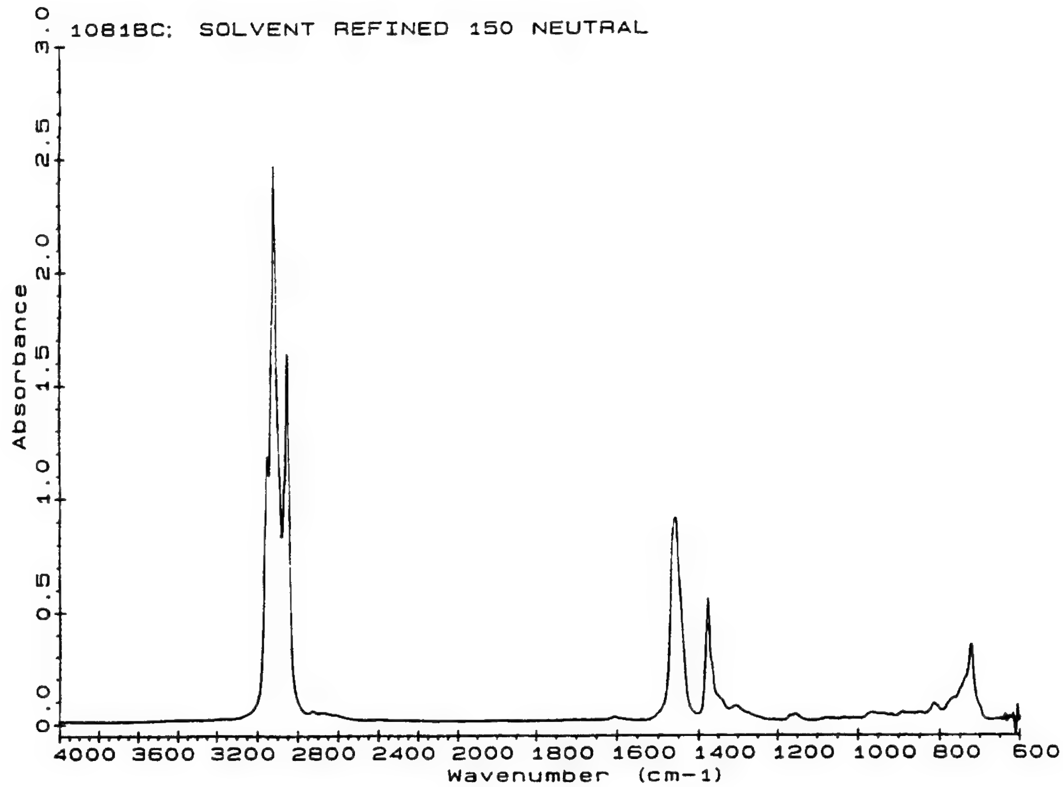

Figure 1. Solvent-refined 150 neutral base stock

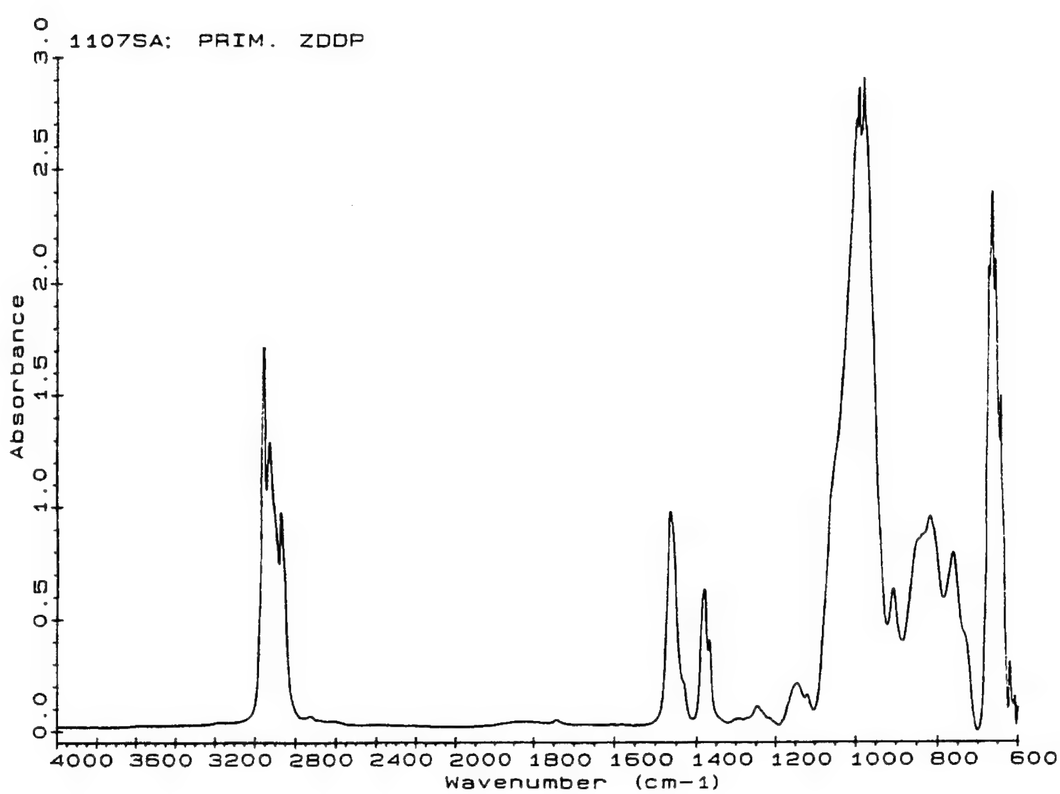

Figure 2. Zinc primary dialkyl dithiophosphate (Prim. ZDDP)

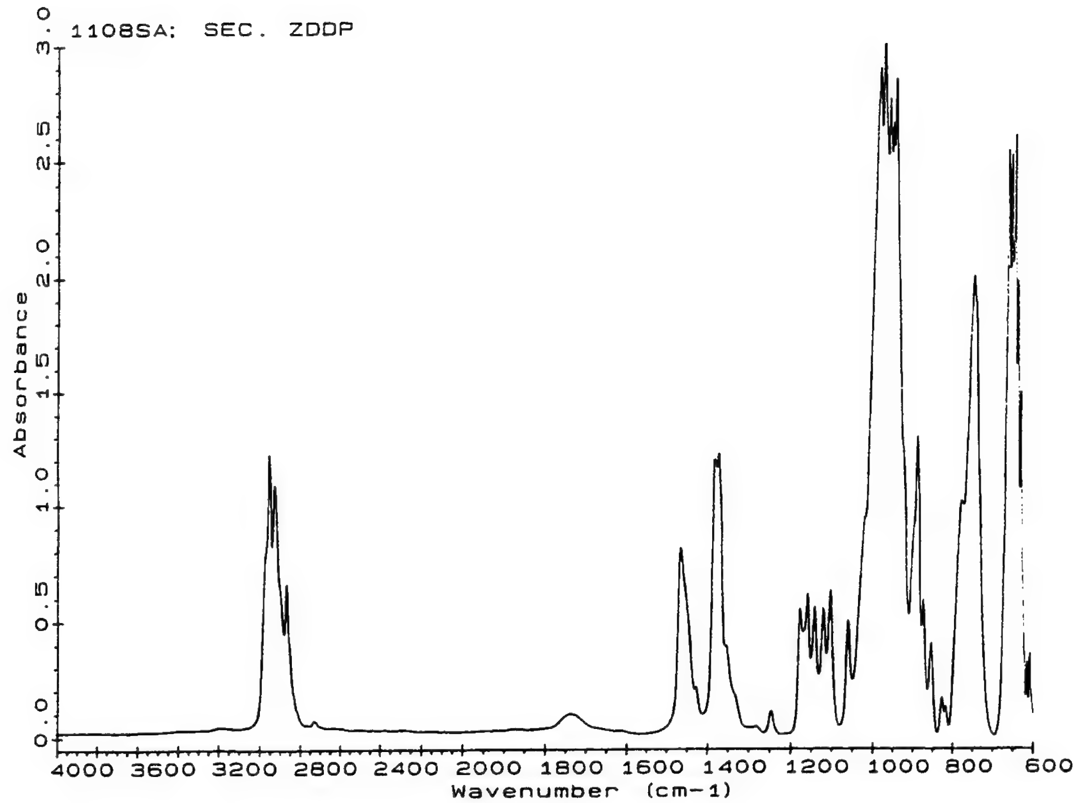

Figure 3. <u>**Zinc secondary dialkyl dithiophosphate (Sec. ZDDP)**</u>

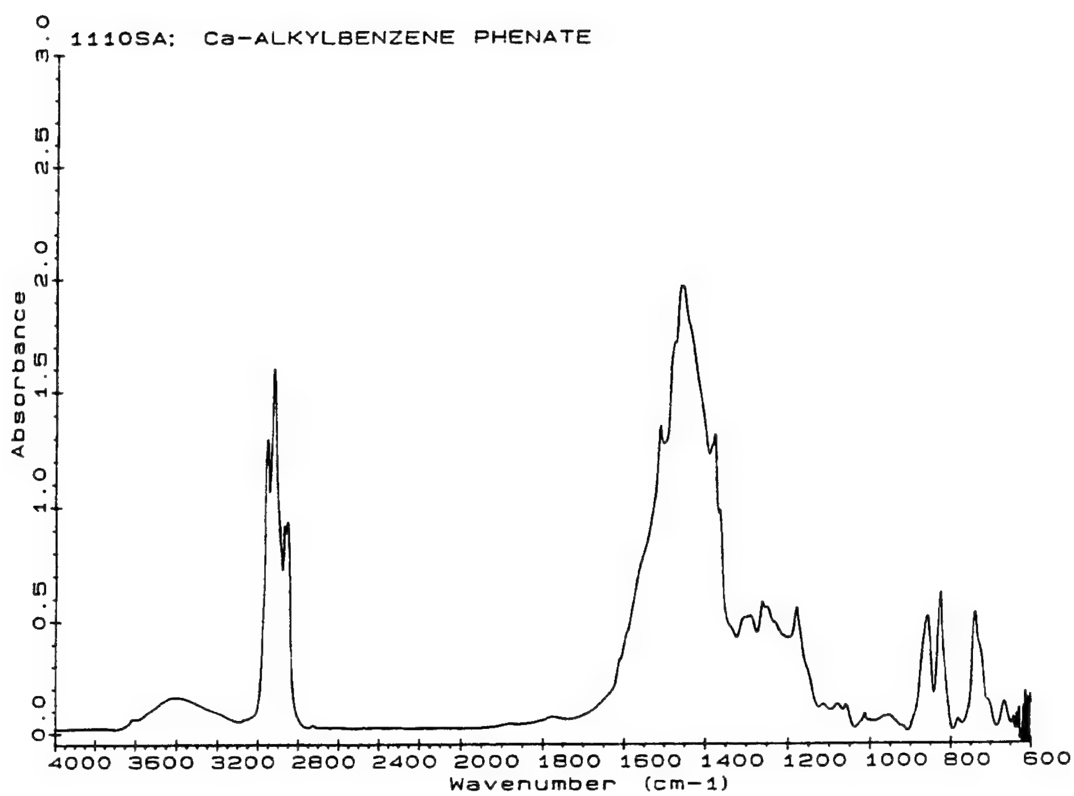

Figure 4. <u>**Calcium alkylbenzene phenate**</u>

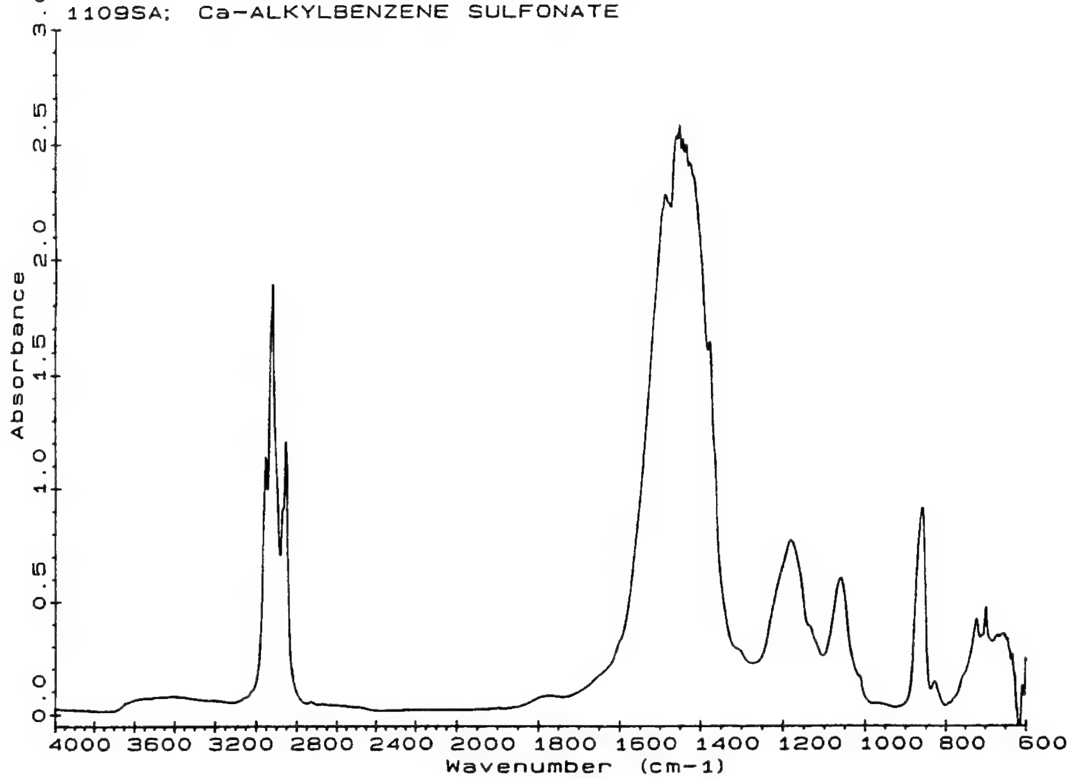

Figure 5. __Calcium alkylbenzene sulfonate__

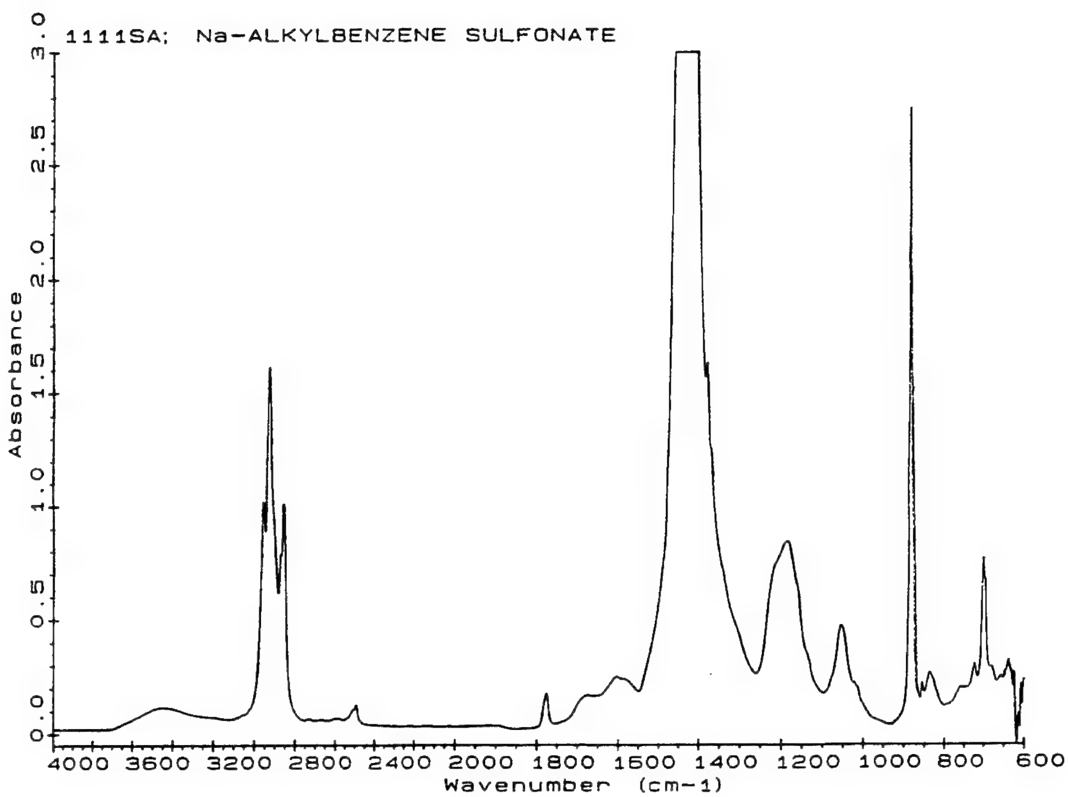

Figure 6. __Sodium alkylbenzene sulfonate__

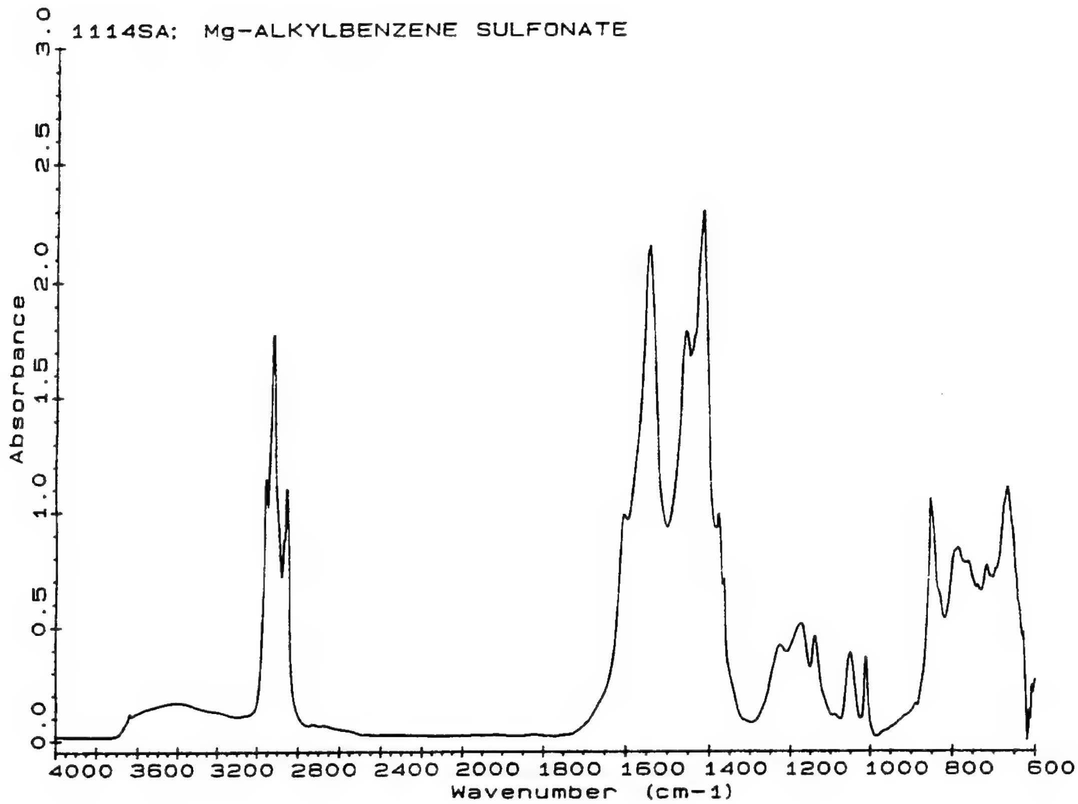

Figure 7. <u>Magnesium alkylbenzene sulfonate</u>

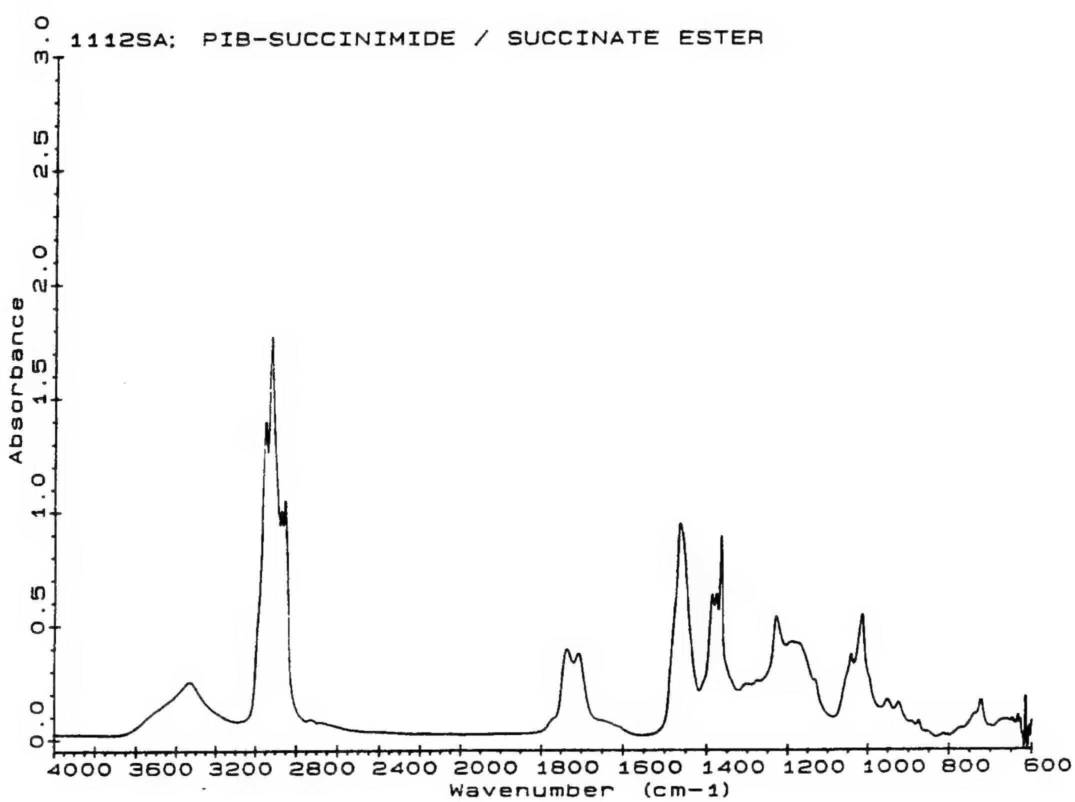

Figure 8. <u>PIB-succinimide/succinate ester</u>

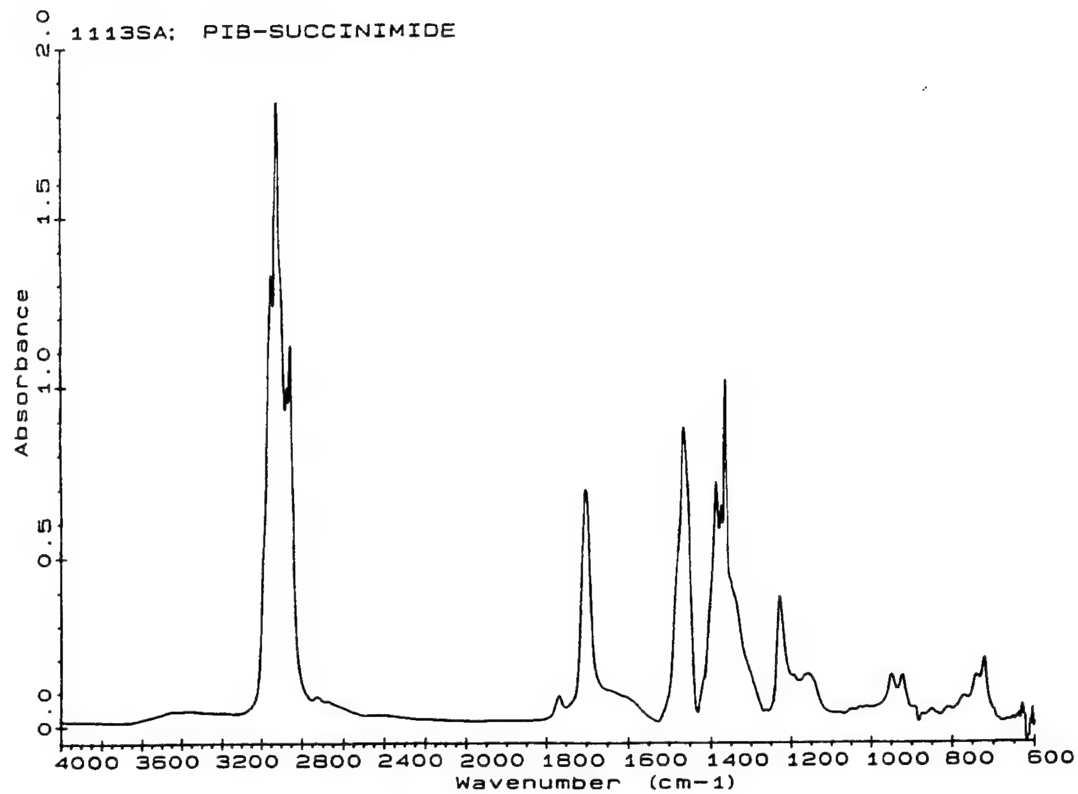

Figure 9. PIB-succinimide

Spectroscopic data were collected on a Nicolet Model 510 FTIR spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector and a horizontal attenuated total reflectance (ATR) zinc selenide cell. Crystal angle of the cell is 45 degrees, with 12 internal reflections through the sample. Depth of beam penetration at 1000 cm^{-1} is 2 µm, resulting in a nominal path length of 0.024 mm. Baseline-corrected FTIR spectra of the average of 32 FTIR scans of each fuel were collected at a resolution of 4 cm^{-1}.

Frequency assignments associated with the various organic chemical groups have been the subject of numerous books, and even computer programs, such as those by Bellamy (14,15), Colthup (16), and Coates (17). Sadtler's (18) "IR Mentor" is a computerized aid to organic functional group identification in infrared spectra.

Some of the characteristic infrared absorption bands of "single" additives may be recognized in these spectra. Bands associated with the P-O-C bonds of ZDDP are located at 920–1050 cm^{-1}, depending upon the nature of the organic portion of the compound. If the C of the P-O-C is part

of a primary alkyl group, then the absorption band will be at 990–1050 cm^{-1}. Secondary alkyl substituents will register at around 960–980 cm^{-1}, while aromatic ZDDP will exhibit an absorption band at around 920–940 cm^{-1}. Characteristic frequency of the P=S bond is around 800–600 cm^{-1}. Sulfonates normally absorb at around 1370 and 1185 cm^{-1}. Carbonates of overbased sulfonates absorb at around 850 and at 1490–1410 cm^{-1}. Succinimides are normally hard to identify through their infrared spectra due to weak absorption bands and the possible overlapping by other components, e.g., carbonyl compounds. Their N-H band is normally located at around 3220, the C=O band as a doublet or triplet between 1750–1670, and the C-N and N-H vibration bands at 1310–1210 cm^{-1}. The most widely used viscosity index improvers are substituted methacrylate esters, or ester amides, absorbing in the 1700–1800 and 1695–1615 cm^{-1} regions, and polyolefins, whose infrared spectra are indistinguishable from base stock hydrocarbon components.

To develop a quantitative spectroscopic method to measure single-additive contents in a lubricant, each of the eight additives was dissolved in the solvent-refined 150 neutral base stock at 1, 5, 10, 15, and 20 wt% concentrations. Baseline-corrected FTIR spectra were obtained on each of these compositions on a zinc selenide ATR cell. For quantitative measurement of the various additives, peak height, instead of area measurements, were carried out at several frequencies to reduce interference by partially overlapping peaks. As a representative set of data, TABLE 1 is presented, in which absorbance values are listed for each major peak of the respective spectra. The data were entered into a spreadsheet and analyzed. Data are graphically presented in Figs. 10 through 17. Presence of both primary and secondary alkyl dithiophosphates may be identified, and their concentrations may be measured at their peaks around 991 and 977 cm^{-1}, respectively. Phenates are exceptionally hard to recognize and measure due to their indistinct infrared spectra. A large peak in the range of 1400–1500 cm^{-1} is diagnostic of the presence of sulfonates. Since sulfonates normally are overbased by inorganic carbonates, e.g., by sodium carbonate, their characteristic bands may be measured at around 875 cm^{-1}. The cations associated with phenates and sulfonates must be identified and measured through elemental analysis. Succinimides are hard to find, but their presence may be suggested by their carbonyl peak at around 1700–1750 and 1350–1400 cm^{-1}.

TABLE 1. Additive Concentration Effects

Additive ID	Wavenumber, cm^{-1}	Absorbance at wt% concentration				
		1	5	10	15	20
1107SA Prim. ZDDP	643	0.0326	0.1284	0.1612	0.2354	0.3143
	663	0.0402	0.2271	0.4047	0.6092	0.7741
	722	0.3348	0.3033	0.3139	0.3213	0.2992
	816	0.0861	0.0660	0.1450	0.1773	0.2122
	991	0.0757	0.2235	0.4233	0.6189	0.7908
	1377	0.6055	0.5731	0.5506	0.5617	0.5599
	1461	0.9502	0.9212	0.9029	0.9152	0.9168
	2854	1.7079	1.6427	1.5967	1.5519	1.5240
	2922	2.4592	2.3094	2.3480	2.2812	2.2921
	2954	1.2492	1.2270	1.2424	1.2619	1.2942
1108SA Sec. ZDDP	637	0.0604	0.1464	0.2423	0.2608	0.4261
	655	0.0652	0.2799	0.5303	0.8429	1.0029
	723	0.3378	0.3343	0.3290	0.3838	0.3336
	750	0.1579	0.2222	0.3029	0.4393	0.4792
	890	0.0577	0.0883	0.1328	0.2056	0.2255
	977	0.1599	0.5727	1.0159	1.4322	1.7993
	1377	0.5648	0.5757	0.6008	0.6160	0.6454
	1461	0.9088	0.8958	0.8872	0.8714	0.8700
	2853	1.6598	1.6206	1.5620	1.5278	1.4735
	2923	2.3901	2.3971	2.2654	2.3062	2.2496
	2954	1.2032	1.2125	1.2007	1.2112	1.2072
1109SA Ca-Alkylbenzene Sulfonate	722	0.3549	0.3236	0.3257	0.3217	0.3175
	1377	0.5601	0.5947	0.6304	0.6759	0.7398
	1458	0.9203	0.9872	1.0598	1.1398	1.2373
	1489	0.1112	0.2066	0.3246	0.4404	0.5796
	2853	1.6689	1.6274	1.5890	1.5682	1.5358
	2922	2.4018	2.4716	2.3428	2.2331	2.2437
	2954	1.1997	1.1972	1.1896	1.1882	1.1857
1110SA Ca-Alkyl Phenate	722	0.3157	0.3008	0.3220	0.3211	0.3121
	1377	0.5534	0.5729	0.6042	0.6262	0.6599
	1458	0.9014	0.9387	0.9912	1.0352	1.0913
	1514	0.0488	0.1090	0.1708	0.2386	0.3117
	2854	1.6202	1.5851	1.5489	1.5316	1.4961
	2921	2.3414	2.3211	2.3388	2.3486	2.2159
	2953	1.1862	1.1806	1.1898	1.2026	1.2024

TABLE 1. Additive Concentration Effects (Cont'd)

Additive ID	Wavenumber, cm^{-1}	Absorbance at wt% concentration				
		1	5	10	15	20
1111SA Na-Alkylbenzene Sulfonate	722	0.3091	0.2914	0.2920	0.3193	0.3184
	883	0.9898	0.2871	0.4553	0.6194	0.7532
	1377	0.5688	0.6008	0.6277	0.6508	0.6872
	1442	0.7381	2.0774	3.1221	7.2920	8.4478
	1445	0.8985	2.0552	2.9046	2.9385	3.5815
	1448	1.0998	1.9024	2.5235	3.2429	3.6238
	2853	1.6391	1.5643	1.5307	1.4862	1.4697
	2923	2.3821	2.3341	2.2641	2.2085	2.1869
	2953	1.2025	1.1832	1.1700	1.1495	1.1505
1112SA PIB-Succinimide/ Succinate Ester	722	0.3436	0.3152	0.2854	0.2728	0.2872
	1367	0.3177	0.3554	0.3929	0.4280	0.4533
	1377	0.6043	0.6167	0.6237	0.6322	0.6305
	1446	1.4019	1.3442	1.3017	1.2980	1.2687
	1454	1.3009	1.3009	1.2836	1.2841	1.2705
	2853	1.5515	1.5374	1.5237	1.4975	1.4739
	2922	2.2983	2.2817	2.2373	2.2337	2.1988
	2954	1.1670	1.1868	1.1965	1.2030	1.2155
1113SA PIB-Succinimide	722	0.3100	0.2828	0.2838	0.2907	0.2710
	1367	0.3431	0.3711	0.4168	0.4423	0.5037
	1377	0.6313	0.6554	0.6368	0.6300	0.6592
	1447	1.2508	1.2750	1.2599	1.2379	1.2658
	1455	1.2673	1.2896	1.2761	1.2595	1.2877
	2853	1.5579	1.5301	1.5275	1.5014	1.4801
	2922	2.2974	2.2672	2.2893	2.2530	2.2205
	2954	1.1732	1.1848	1.1975	1.2022	1.2032
1114SA Mg-Alkylbenzene Sulfonate	722	0.2921	0.3160	0.3029	0.3343	0.2815
	855	0.0567	0.0796	0.1322	0.1726	0.2152
	1377	0.6424	0.6533	0.6927	0.6836	0.7478
	1444	1.1640	1.2778	1.3739	1.4291	1.4593
	1455	1.2562	1.3045	1.3798	1.4080	1.4686
	1517	0.0955	0.1393	0.2189	0.2417	0.3270
	1550	0.0752	0.1775	0.3338	0.4301	0.5917
	1606	0.0541	0.1078	0.1848	0.2342	0.3302
	2853	1.5487	1.5412	1.5242	1.5030	1.4876
	2922	2.2966	2.3055	2.3189	2.2657	2.2581
	2953	1.1707	1.1718	1.1724	1.1742	1.1718

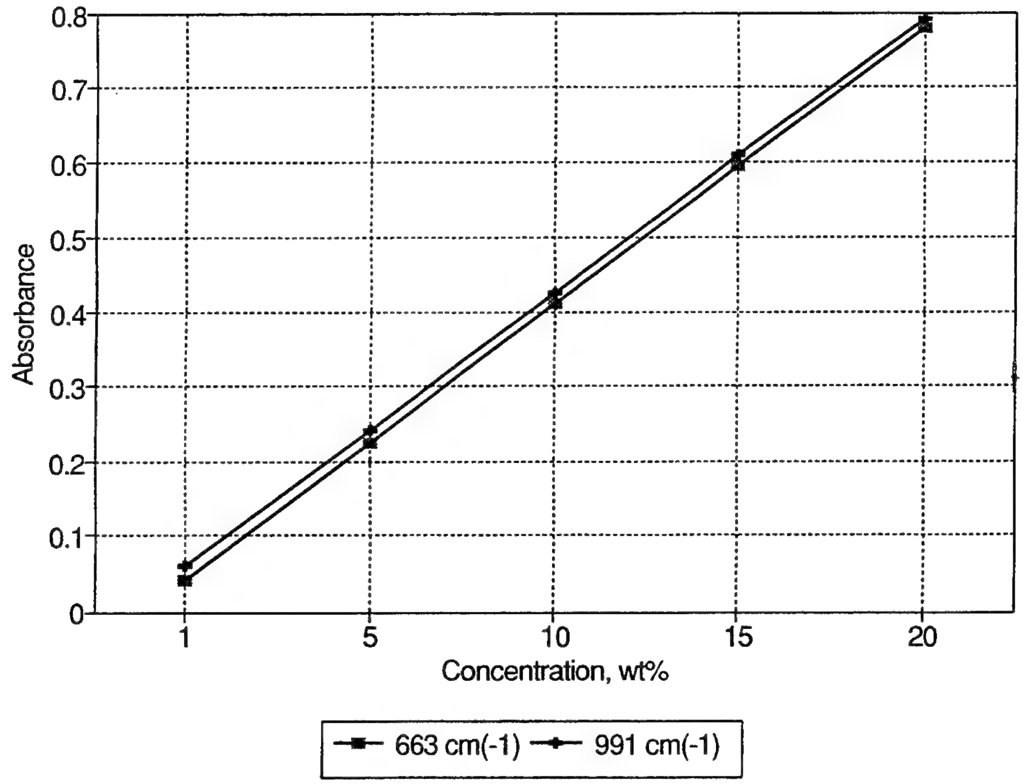

Figure 10. <u>**Calibration curves for zinc primary dialkyl dithiosphosphate, No. 1107SA**</u>

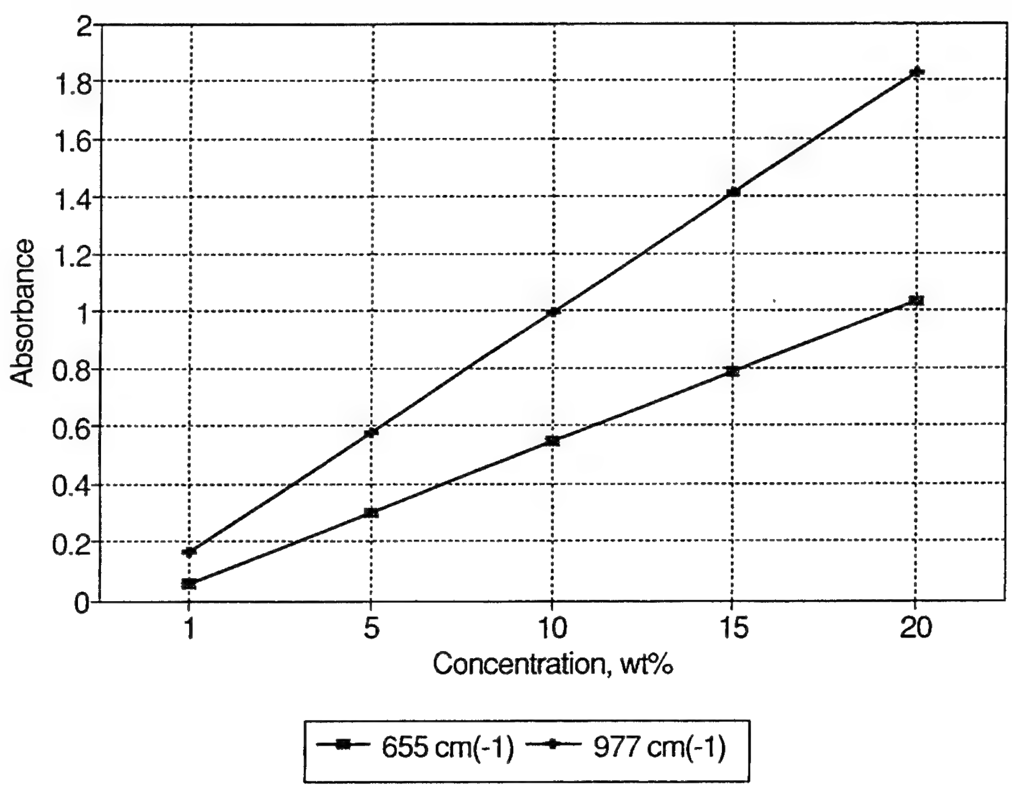

Figure 11. <u>**Calibration curves for zinc secondary dialkyl dithiophosphate, No. 1108SA**</u>

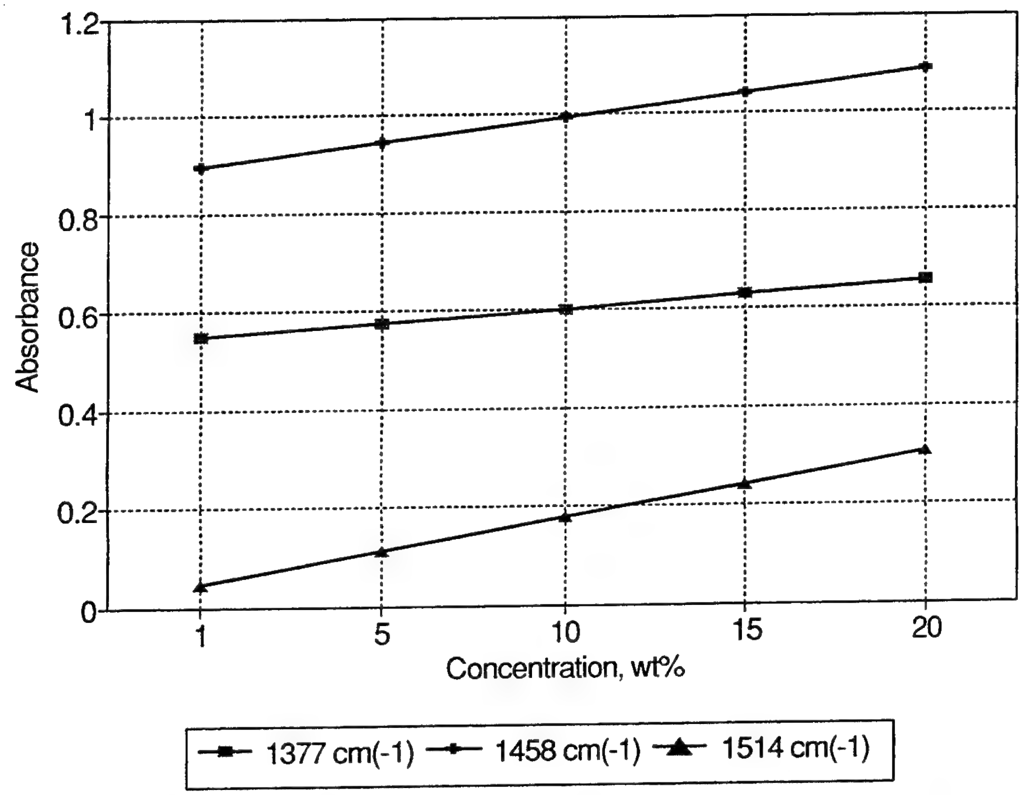

Figure 12. <u>**Calibration curves for calcium alkylbenzene phenate, No. 1110SA**</u>

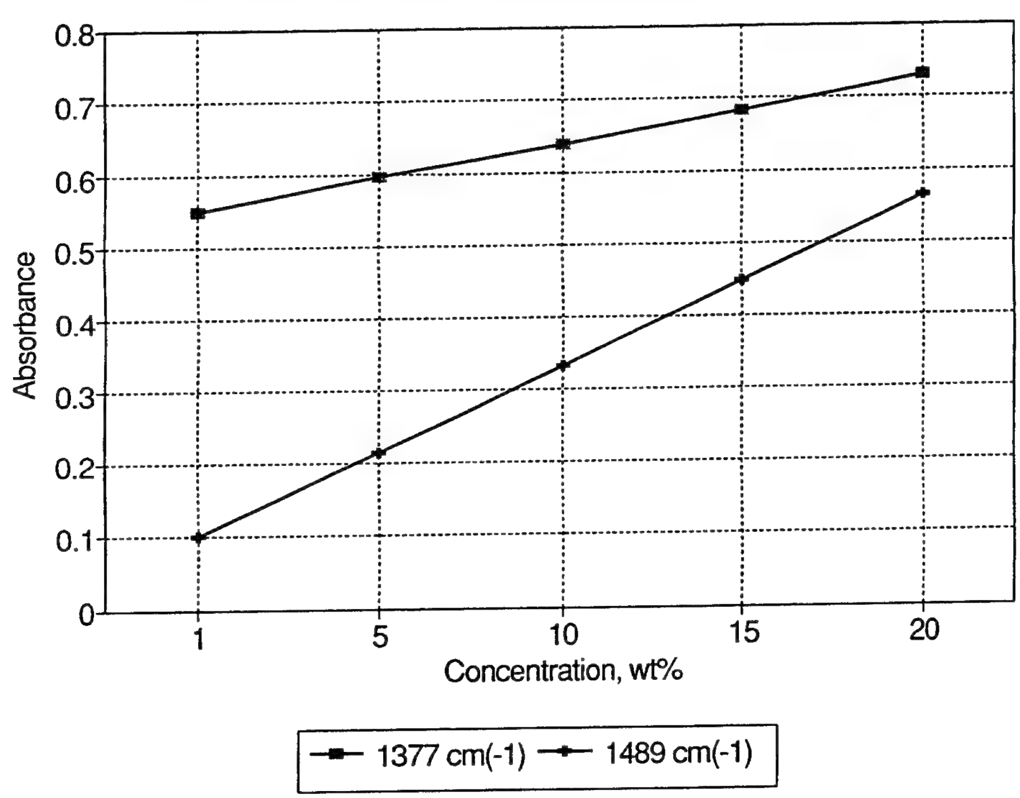

Figure 13. <u>**Calibration curves for calcium alkylbenzene sulfonate, No. 1109SA**</u>

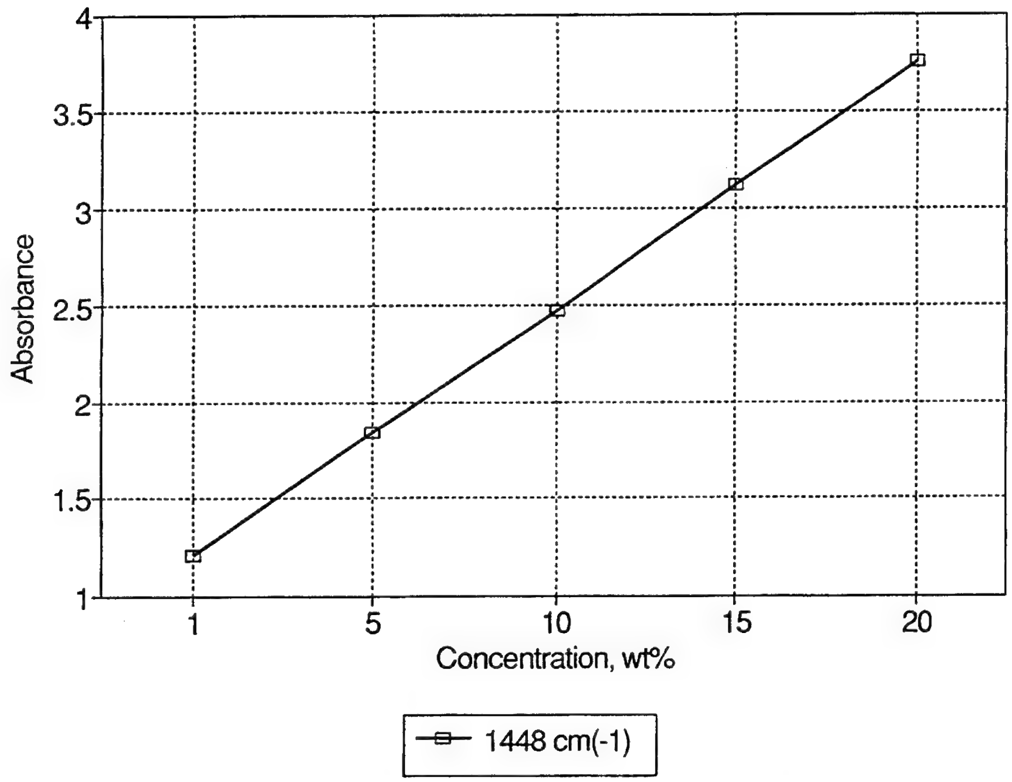

Figure 14. <u>Calibration curves for sodium alkylbenzene sulfonate, No. 1111SA</u>

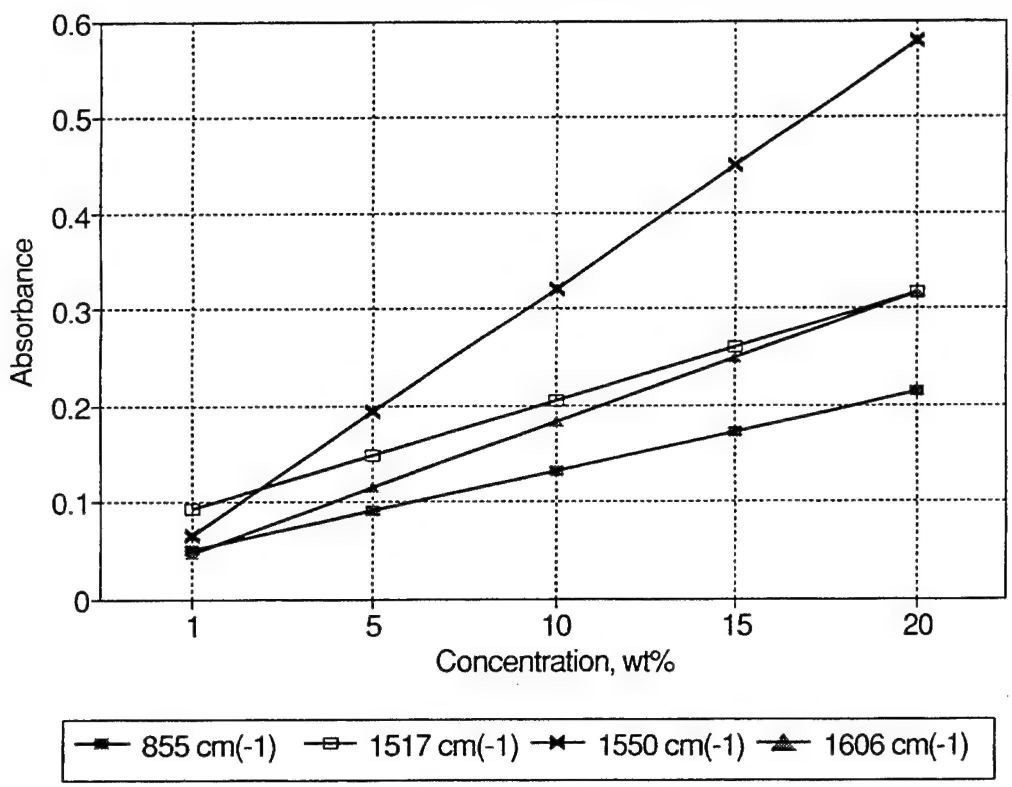

Figure 15. <u>Calibration curves for magnesium alkylbenzene sulfonate, No. 1114SA</u>

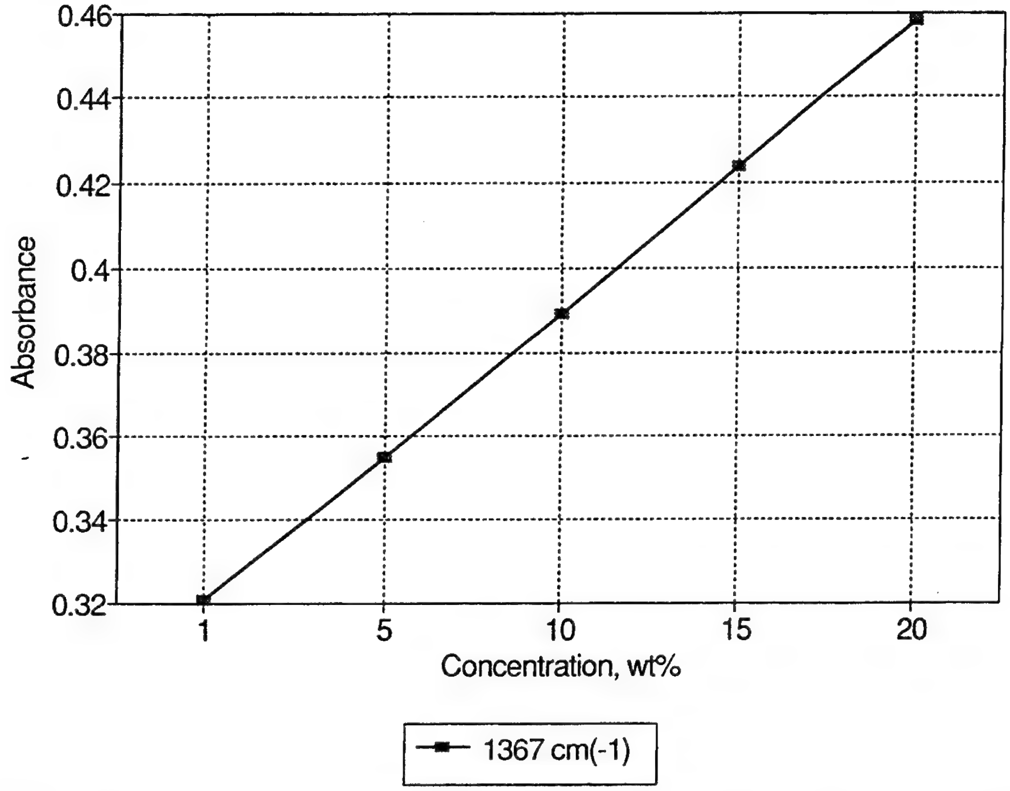

Figure 16. Calibration curves for PIB-succinimide/succinate ester, No. 1112SA

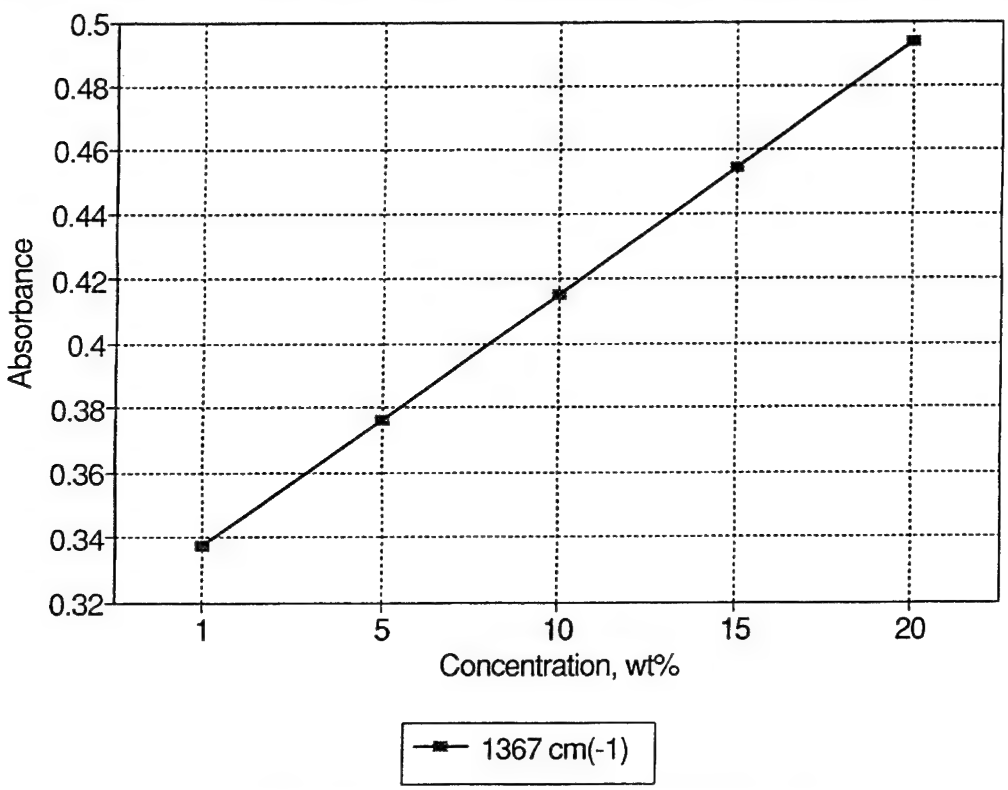

Figure 17. Calibration curves for PIB-succinimide, No. 1113SA

As demonstrated, in lubricant compositions comprising the studied concentration ranges of single additives, quantitative measurement of their concentrations may be accomplished using FTIR spectroscopy. Application of the same measurement technique has not yet been extended to the full useful concentration ranges of key members of several of the more important additive packages in finished lubricants. Further development in these studies, in conjunction with elemental analysis, is expected to lead to a good estimation of additive treatment and additive depletions in lubricants.

5. Analytical Chemical Protocol for New Oil Characterization

It is a natural objective of any study to attempt to gain the most information about a sample with a minimum number of experiments. Attempts have been made to identify several critical lubricant properties that related to key performance parameters. Further studies, through establishing correlations among the measured properties, attempted to reduce the required number of analyses. Jenkins (19) studied the significance and interdependence of inspection tests of lubricating oils. He noted that it is possible to reduce the number of measurements while maximizing the number of obtained product property values by taking into account the various relationships that exist among normally measured physical chemical properties. Jenkins concluded that of the 23 tests considered, only three were associated with independent properties. These independent properties were found to be the neutralization number, pour point, and nitrogen content. Jenkins also noted that "examination of the lubricating oil base stock data suggests that the bulk properties may be efficiently characterized by the specific gravity, kinematic viscosity at 100° and 210°F, and the sulfur content."

The suitability of a lubricant to perform satisfactorily under given engine conditions may be assessed several ways. The lubricant's performance may be measured in an operating engine; through measurement of properties that are known to correlate to performance under operating engine conditions; or correlating an unknown lubricant's composition to the composition of a lubricant whose performance is known. Depending upon the immediate requirements, a selection may be made for the appropriate evaluating experimental tools. The following options have been investigated for possible adaptation for military field applications.

If the analytical requirement is restricted to quickly determining the emergency suitability of an oil for an application, determination of a limited number of experiments is warranted, e.g., measurement of the product's acid number, density, and kinematic viscosity measured at possibly two temperatures. Commercially available equipment, ruggedized for military applications, may perform each of these measurements. The equipment could be integrated in such a way that the operator would need only to introduce the lubricant into the sample inlet of the instrument cluster, and the built-in computer operated system would direct an aliquot of the sample to the various individual instruments to perform the measurements. Upon completion of the measurements, the printed results could also include the allowed or recommended property values.

Analysis of lubricants in a future petroleum laboratory may be categorized into a simpler and a more complex areas. <u>The simpler scenario</u> is one in which the unknown lubricant is included in an available data base of products. This data base would include several selected property values of known lubricants, as well as fingerprints of the products by FTIR and by a high-temperature gas chromatographic procedure. A simple confirmation of lubricant identity of an unknown lubricant could be achieved by obtaining an FTIR spectrum of the product, and allowing the equipment's built-in library to find the matching known product. All library search softwares include a descriptor, occasionally called the HQI or "hit quality index," that expresses the "goodness of fit" between the spectra of the known and unknown products. If the fit is within the acceptable range, the probability is high that the known and unknown samples are essentially identical. Confirmation of this preliminary finding should be secured by a second test, e.g., elemental analysis and/or high-temperature gas chromatography. Matching data between those measured on the unknown sample and those in the library may be taken as proofs that the unknown sample is <u>essentially identical</u> to the known sample of the library.

The analytical problem becomes substantially <u>more complex</u> if a match cannot be found in the library for the unknown lubricant's FTIR spectrum. To achieve some measure of characterization of such a lubricant, a tentative experimental protocol was designed, based upon the utilization of an integrated set of instruments. The instruments are expected to be interfaced through a computer and programmed to perform the required analyses without the need for highly trained

operators. Such a system is expected to yield data that may be automatically compared by the computer to a data base that also includes a set of lubricant specifications. The information would identify similarities between the unknown lubricant and those in the data base. Such similarity would suggest possible safe uses for the unknown product. Since results of the instrumental analyses may be compared to data obtained from engine tests and bench or rig tests, this work may also lead to the development of methods that may predict engine performance parameters from the less expensive, more timely, and more repeatable chemical compositional data.

In the present experimental protocol, the compositional analysis of the various products includes elemental analysis, midband FTIR spectroscopy, HPLC in its gel permeation chromatographic (GPC) mode, and high-temperature gas chromatography (HTGC). This set of instruments would be operated and the results evaluated by a dedicated on-board computer, requiring only minimal interfacing with a petroleum laboratory specialist. Alternately, the raw data from the instrument cluster may be transferred through an appropriate linkage, e.g., satellite, to a central processing facility, which would return the processed data to the military commander.

Contributing factors for the selection of these instrumental techniques are summarized in the following paragraphs:

- Elemental analysis characterizes the overall composition and reveals and measures certain additives in the products.

- FTIR spectroscopy reveals major compositional information and the presence of some additives. Characterization or "fingerprinting" of the composition and development of quantitative measurement of the several additives' concentrations are promising.

- The GPC mode of HPLC detects the presence of polymers and evaluates the products' molecular weight range. This procedure can, for example, detect the presence of polymeric viscosity index improver(s) and characterize their molecular weight range. A representative GPC calibration curve, using poly-styrene standards, is shown in

Fig. 18. GPC gave interesting data with respect to polymer distribution in the finished lubricants. It was shown, for example, that some lubricant compositions contain up to three different polymers or polymers having up to three different molecular sizes. These polymers' concentrations may presently be measured only by the laborious procedure of weighing the preparative-scale GPC separated fractions. While chemical characterization of the same fractions may be aided by FTIR spectroscopy, such analytical expertise is not recommended for routine military laboratory applications.

- Boiling point distribution (BPD) by HTGC indicates compositional and molecular weight information. Determination of the boiling point distribution of the finished lubricants and lubricant base stocks may be accomplished using modified ASTM D 2880 procedures.

Each of the selected methods may furnish results in a digitized fashion, amenable to computerized storage, search, and retrieval. A computerized data base was partially developed to track, manipulate, sort, and retrieve the data.

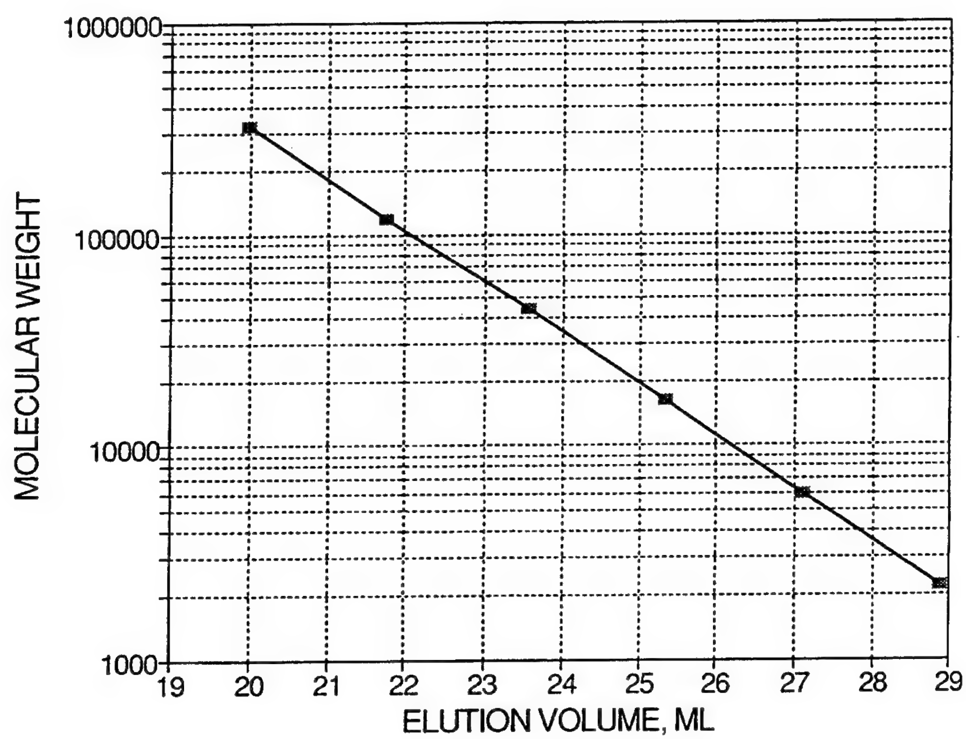

Figure 18. <u>GPC calibration to poly-styrene</u>

While a final experimental protocol has not yet been established, during the course of this project, a working or tentative analytical chemical protocol was developed and is being upgraded as new information warrants. Present experimental protocol does not address the detection and destruction of antimaterial agents. Such analyses require highly specific knowledge of the possible agents, followed by design of specific analytical tools to detect them.

IV. CONCLUSIONS AND RECOMMENDATIONS

In assessing a commercial used oil analysis method, it was concluded that the FTIR-based used oil analysis method should be used only within the scope of its design, i.e., for trend analysis in a well-regulated fleet of vehicles in which the lubricant and the fuel are known and controlled. Since these criteria are not fulfilled under normal field operations, and especially under battlefield conditions, this commercial analytical method should not be used by the U.S. Army, since furnishing misleading data under any condition is considered <u>worse</u> than providing no data at all. If this commercial program is to be used under nontrend analysis conditions, that is, conditions for which it was not designed, the program must be modified. It is **recommended** that the software be used only after extensive modifications that would allow the incorporation of samples of the new lubricant and the specific fuel used in the vehicle as appropriate spectral reference materials. However, it is unlikely that such samples will be available from Army vehicles under battlefield conditions. If these inputs were accessible to the program, the computer may calculate data useful in aiding engine maintenance.

Efforts were made to characterize and identify lubricants through instrumental analyses, including spectroscopic fingerprinting and the establishment of FTIR spectral libraries. To increase the usefulness of the results of FTIR spectra libraries, data bases have been constructed to include all known specification and inspection data. If FTIR spectra of all possible acceptable lubricant samples were to be included in a spectral library, any later generation sample of the same lubricant may be properly identified by simply establishing spectral identities through library searches. Therefore, it is **recommended** that the Armed Forces in general, and the Army specifically, should augment documentation of each purchase of lubricants with standardized

FTIR spectroscopic fingerprinting procedure, in addition to the traditionally determined lubricant property values, and retain all information for convenient computer retrieval for ready comparison with instrumental analytical data on future unknown samples.

It was shown that the concentration of several widely used lubricant additives may be measured in their base stocks using FTIR spectroscopy. Application of this measurement technique has not yet been extended to the full useful concentration ranges of key members of the more important additive packages in finished lubricants. Further development in these studies is **recommended,** in conjunction with elemental analysis, to arrive at reasonable estimations of additive loadings and additive depletions in lubricants.

Several increasingly complex experimental protocols were suggested to characterize finished lubricants. While a final experimental protocol was not established during the course of this project, a working or tentative analytical chemical protocol was developed. In the latest, relatively complex experimental protocol, the analysis of the various products includes elemental analysis, midband FTIR spectroscopy, high-performance liquid chromatography (HPLC) in its gel permeation chromatographic (GPC) mode, and high-temperature gas chromatography (HTGC). This integrated set of instruments would be operated and the results evaluated by a dedicated on-board computer, requiring only minimal interfacing with a petroleum laboratory specialist. Alternately, the raw data from the instrument cluster may be transferred through an appropriate linkage, e.g., satellite, to a central processing facility, which would then return the processed data to the military commander. It is **recommended** that the lubricant additive industry, key analytical instrument manufacturers, and researchers representing the Armed Forces pool their resources to solve the problem.

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PETROLEUM STAFF ANALYST
PENTAGON
WASHINGTON DC 20301-8000

ODUSD
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400 ARMY NAVY DR
STE 206
ARLINGTON VA 22202

HQ USEUCOM
ATTN: ECJU L1J 1
UNIT 30400 BOX 1000
APO AE 09128-4209

US CINCPAC
ATTN: J422 BOX 64020 1
CAMP H M SMITH
HI 96861-4020

JOAP TSC 1
BLDG 780
NAVAL AIR STA
PENSACOLA FL 32508-5300

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DLA MMSB 1
CAMERON STA
ALEXANDRIA VA 22304-6100

CDR
DEFENSE FUEL SUPPLY CTR
ATTN: DFSC Q BLDG 8 1
DFSC S BLDG 8 1
CAMERON STA
ALEXANDRIA VA 22304-6160

CDR
DEFENSE GEN SUPPLY CTR
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DGSC STA 1
8000 JEFFERSON DAVIS HWY
RICHMOND VA 23297-5678

DIR ADV RSCH PROJ AGENCY
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3701 N FAIRFAX DR
ARLINGTON VA 22203-1714

Department of the Army

HQDA
ATTN: DALO TSE 1
DALO SM 1
PENTAGON
WASHINGTON DC 20310-0103

SARDA
ATTN: SARD TL 1
PENTAGON
WASHINGTON DC 20310-0103

CDR AMC
ATTN: AMCRD S 1
AMCRD E 1
AMCRD IM 1
AMCRD IT 1
AMCEN A 1
AMCLG MS 1
AMCLG MT 1
AMCICP ISI 1
5001 EISENHOWER AVE
ALEXANDRIA VA 22333-0001

TARDEC
ATTN: AMSTA CMA 1
AMSTA CMB 1
AMSTA CME 1
AMSTA HBM 1
AMSTA N 1
AMSTA R 1
AMSTA RG 1
AMCPM ATP 1
AMSTA Q 1
AMSTA UE 1
AMSTA UG 1
CDR TACOM
WARREN MI 48397-5000

CDR ARMY TACOM
ATTN: AMSTA FP 1
AMSTA KL 1
AMSTA MM 1
AMSTA MT 1
AMSTA MC 1
AMSTA GT 1
AMSTA FNG 1
AMSTA FR 1
USMC LNO 1
AMCPM LAV 1
AMCPM M 113/M60 1
AMCPM CCE/SMHE 1
WARREN MI 48397-5000

DEPARTMENT OF THE ARMY
MOBILITY TECH CTR BELVOIR
ATTN: AMSTA RBF (M E LEPERA) 10
AMSTA RBXA (R E TOBEY) 1
10115 GRIDLEY RD STE 128
FT BELVOIR VA 22060-5843

PROG EXEC OFFICER
ARMORED SYS MODERNIZATION
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SFAE ASM BV 1
SFAE ASM CV 1
SFAE ASM AG 1
CDR TACOM
WARREN MI 48397-5000

PROG EXEC OFFICER
ARMORED SYS MODERNIZATION
ATTN: SFAE ASM FR 1
SFAE ASM AF 1
PICATINNY ARSENAL NJ 07806-5000

PROG EXEC OFFICER
COMBAT SUPPORT
ATTN: SFAE CS TVL 1
SFAE CS TVM 1
SFAE CS TVH 1
CDR TACOM
WARREN MI 48397-5000

PROG EXEC OFFICER
ARMAMENTS
ATTN: SFAE AR HIP 1
SFAE AR TMA 1
PICATINNY ARSENAL NJ 07806-5000

PROG MGR
UNMANNED GROUND VEH
ATTN: AMCPM UG 1
REDSTONE ARSENAL AL 35898-8060

DIR
ARMY RSCH LAB
ATTN: AMSRL CP PW 1
2800 POWDER MILL RD
ADELPHIA MD 20783-1145

VEHICLE PROPULSION DIR
ATTN: AMSRL VP (MS 77 12) 1
NASA LEWIS RSCH CTR
21000 BROOKPARK RD
CLEVELAND OH 44135

CDR AMSAA
ATTN: AMXSY CM 1
AMXSY L 1
APG MD 21005-5071

CDR ARO
ATTN: AMXRO EN (D MANN) 1
RSCH TRIANGLE PK
NC 27709-2211

DIR
AMC PKG STO CONT CTR
ATTN: SDSTO TE S 1
TOBYHANNA PA 18466-5097

CDR AEC
ATTN: SFIM AEC ECC (T ECCLES) 1
APG MD 21010-5401

CDR ARMY ATCOM
ATTN: AMSAT I ME (L HEPLER) 1
AMSAT I LA (V SALISBURY) 1
AMSAT R EP (V EDWARD) 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR AVIA APPL TECH DIR
ATTN: AMSAT R TP (H MORROW) 1
FT EUSTIS VA 23604-5577

CDR ARMY NRDEC
ATTN: SATNC US (J SIEGEL) 1
SATNC UE 1
NATICK MA 01760-5018

CDR ARMY ARDEC
ATTN: SMCAR CC 1
SMCAR ESC S 1
PICATINNY ARSENAL NJ 07808-5000

CDR ARMY DESCOM
ATTN: AMSDS MN 1
AMSDS EN 1
CHAMBERSBURG PA 17201-4170

CDR ARMY AMCCOM
ATTN: AMSMC MA 1
ROCK ISLAND IL 61299-6000

CDR ARMY WATERVLIET ARSN
ATTN: SARWY RDD 1
WATERVLIET NY 12189

DIR AMC LOG SPT ACT
ATTN: AMXLS LA 1
REDSTONE ARSENAL AL 35890-7466

CDR APC
ATTN: SATPC Q 1
SATPC QE (BLDG 85 3) 1
NEW CUMBERLAND PA 17070-5005

PETROL TEST FAC WEST 1
BLDG 247 TRACEY LOC
DDRW
P O BOX 96001
STOCKTON CA 95296-0960

CDR ARMY LEA
ATTN: LOEA PL 1
NEW CUMBERLAND PA 17070-5007

CDR ARMY TECOM
ATTN: AMSTE TA R 1
AMSTE TC D 1
AMSTE EQ 1
APG MD 21005-5006

PROG MGR PETROL WATER LOG
ATTN: AMCPM PWL 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

PROG MGM MOBILE ELEC PWR
ATTN: AMCPM MEP 1
7798 CISSNA RD STE 200
SPRINGFIELD VA 22150-3199

CDR
ARMY COLD REGION TEST CTR
ATTN: STECR TM 1
STECR LG 1
APO AP 96508-7850

CDR
ARMY BIOMED RSCH DEV LAB
ATTN: SGRD UBZ A 1
FT DETRICK MD 21702-5010

CDR FORSCOM
ATTN: AFLG TRS 1
FT MCPHERSON GA 30330-6000

CDR TRADOC
ATTN: ATCD SL 5 1
INGALLS RD BLDG 163
FT MONROE VA 23651-5194

CDR ARMY ARMOR CTR
ATTN: ATSB CD ML 1
ATSB TSM T 1
FT KNOX KY 40121-5000

CDR ARMY QM SCHOOL
ATTN: ATSM CD 1
ATSM PWD 1
FT LEE VA 23001-5000

ARMY COMBINED ARMS SPT CMD
ATTN: ATCL CD 1
ATCL MS 1
FT LEE VA 23801-6000

CDR ARMY FIELD ARTY SCH
ATTN: ATSF CD 1
FT SILL OK 73503

CDR ARMY TRANS SCHOOL
ATTN: ATSP CD MS 1
FT EUSTIS VA 23604-5000

CDR ARMY INF SCHOOL
ATTN: ATSH CD 1
ATSH AT 1
FT BENNING GA 31905-5000

CDR ARMY AVIA CTR
ATTN: ATZQ DOL M 1
ATZQ DI 1
FT RUCKER AL 36362-5115

CDR ARMY CACDA
ATTN: ATZL CD 1
FT LEAVENWORTH KA 66027-5300

CDR ARMY ENGR SCHOOL
ATTN: ATSE CD 1
FT LEONARD WOOD
MO 65473-5000

CDR ARMY ORDN CTR
ATTN: ATSL CD CS 1
APG MD 21005

CDR ARMY SAFETY CTR
ATTN: CSSC PMG 1
CSSC SPS 1
FT RUCKER AL 36362-5363

CDR ARMY CSTA
ATTN: STECS EN 1
STECS LI 1
STECS AE 1
STECS AA 1
APG MD 21005-5059

CDR ARMY YPG
ATTN: STEYP MT TL M 1
YUMA AZ 85365-9130

CDR ARMY CERL
ATTN: CECER EN 1
P O BOX 9005
CHAMPAIGN IL 61826-9005

DIR 1
AMC FAST PROGRAM
10101 GRIDLEY RD STE 104
FT BELVOIR VA 22060-5818

CDR I CORPS AND FT LEWIS
ATTN: AFZH CSS 1
FT LEWIS WA 98433-5000

CDR
RED RIVER ARMY DEPOT
ATTN: SDSRR M 1
SDSRR Q 1
TEXARKANA TX 75501-5000

PS MAGAZINE DIV
ATTN: AMXLS PS 1
DIR LOGSA
REDSTONE ARSENAL AL 35898-7466

CDR 6TH ID (L)
ATTN: APUR LG M 1
1060 GAFFNEY RD
FT WAINWRIGHT AK 99703

Department of the Navy

OFC OF NAVAL RSCH
ATTN: ONR 464 1
800 N QUINCY ST
ARLINGTON VA 22217-5660

CDR
NAVAL SEA SYSTEMS CMD
ATTN: SEA 03M3 1
2531 JEFFERSON DAVIS HWY
ARLINGTON VA 22242-5160

CDR
NAVAL SURFACE WARFARE CTR
ATTN: CODE 632 1
CODE 859 1
3A LEGGETT CIRCLE
ANNAPOLIS MD 21401-5067

CDR
NAVAL RSCH LABORATORY
ATTN: CODE 6181 1
WASHINGTON DC 20375-5342

CDR
NAVAL AIR WARFARE CTR
ATTN: CODE PE33 AJD 1
P O BOX 7176
TRENTON NJ 08628-0176

CDR 1
NAVAL PETROLEUM OFFICE
CAMERON STA T 40
5010 DUKE STREET
ALEXANDRIA VA 22304-6180

OFC ASST SEC NAVY (I & E) 1
CRYSTAL PLAZA 5
2211 JEFFERSON DAVIS HWY
ARLINGTON VA 22244-5110

CDR
NAVAL AIR SYSTEMS CMD
ATTN: AIR 53623C 1
1421 JEFFERSON DAVIS HWY
ARLINGTON VA 22243-5360

Department of the Navy/U.S. Marine Corps

HQ USMC
ATTN: LPP 1
WASHINGTON DC 20380-0001

PROG MGR COMBAT SER SPT 1
MARINE CORPS SYS CMD
2033 BARNETT AVE STE 315
QUANTICO VA 22134-5080

PROG MGR GROUND WEAPONS 1
MARINE CORPS SYS CMD
2033 BARNETT AVE
QUANTICO VA 22134-5080

PROG MGR ENGR SYS 1
MARINE CORPS SYS CMD
2033 BARNETT AVE
QUANTICO VA 22134-5080

CDR
MARINE CORPS SYS CMD
ATTN: SSE 1
2030 BARNETT AVE STE 315
QUANTICO VA 22134-5010

CDR
BLOUNT ISLAND CMD
ATTN: CODE 922/1 1
5880 CHANNEL VIEW BLVD
JACKSONVILLE FL 32226-3404

CDR
MARINE CORPS LOGISTICS BA
ATTN: CODE 837 1
814 RADFORD BLVD
ALBANY GA 31704-1128

CDR 1
2ND MARINE DIV
PSC BOX 20090
CAMP LEJEUNNE NC 28542-0090

CDR 1
1ST MARINE DIV
CAMP PENDLETON CA 92055-5702

CDR 1
FMFPAC G4
BOX 64118
CAMP H M SMITH
HI 96861-4118

Department of the Air Force

HQ USAF/LGSSF
ATTN: FUELS POLICY 1
1030 AIR FORCE PENTAGON
WASHINGTON DC 20330-1030

HQ USAF/LGTV
ATTN: VEH EQUIP/FACILITY 1
1030 AIR FORCE PENTAGON
WASHINGTON DC 20330-1030

AIR FORCE WRIGHT LAB
ATTN: WL/POS 1
WL/POSF 1
WL/POSL 1
1790 LOOP RD N
WRIGHT PATTERSON AFB
OH 45433-7103

AIR FORCE WRIGHT LAB
ATTN: WL/MLBT 1
2941 P ST STE 1
WRIGHT PATTERSON AFB
OH 45433-7750

AIR FORCE WRIGHT LAB
ATTN: WL/MLSE 1
2179 12TH ST STE 1
WRIGHT PATTERSON AFB
OH 45433-7718

AIR FORCE MEEP MGMT OFC 1
615 SMSQ/LGTV MEEP
201 BISCAYNE DR STE 2
ENGLIN AFB FL 32542-5303

SA ALC/SFT 1
1014 ANDREWS RD STE 1
KELLY AFB TX 78241-5603

WR ALC/LVRS 1
225 OCMULGEE CT
ROBINS AFB
GA 31098-1647

Other Federal Agencies

NASA LEWIS RESEARCH CENTER CLEVELAND OH 44135	1	DOE CE 151 (MR RUSSELL) 1000 INDEPENDENCE AVE SW WASHINGTON DC 20585	1
NIPER PO BOX 2128 BARTLESVILLE OK 74005	1	EPA AIR POLLUTION CONTROL 2565 PLYMOUTH RD ANN ARBOR MI 48105	1
DOT FAA AWS 110 800 INDEPENDENCE AVE SW WASHINGTON DC 20590	1		